PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-001316

(43)Date of publication of application : 06.01.1998

(51)Int.Cl.

C01G 51/00
C01G 53/00
C01G 55/00
H01M 4/04
H01M 4/58
H01M 10/40

(21)Application number : 08-171755

(22)Date of filing : 10.06.1996

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(54) LITHIUM-COBALT MULTIPLE OXIDE AND PRODUCTION THEREOF, AND LITHIUM ION SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain multiple oxide particle suitable for a positive electrode activating material for Li ion secondary battery by dispersing cobalt hydroxide being trivalent cobalt oxyhydroxide and a specific compound into a lithium hydroxide aqueous liquid and rejecting to heat treatment.
SOLUTION: At least one kind between cobalt and cobalt hydroxide oxyhydroxide, each having trivalent valency and a compound at least one kind element among B, Mg, Si, Cu, Cy, Y, Ti, V, Mn, Fe, Ni, Sn, Zr, Sb, Nb, Ru, Pb, Hf, Ta, La, Pr, and Nd are dispersed into the Li hydroxide aqueous liquid and heated to obtain the object complex oxide particles. The Li-Co multiple oxide particle is submicron size and has narrow particle distribution, large specific surface area and a uniform composition.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

* NOTICES *

JP 10-001316

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] The following general formula (1);.
LiCo1-x Ax Oy (1)
(x express the rational number of 0-0.25 among a formula.) y expresses the rational number of 1.875-2.25. A B, Mg, Si, Cu, Ce, Y, Ti, V, Mn, Fe, nickel, at least one sort of elements chosen from the group which consists of Sn, Zr, Sb, Nb, Ru, Pb, Hf, Ta, La, Pr, and Nd are expressed The lithium cobalt multiple-oxide particle to which it consists of a lithium cobalt multiple oxide expressed, and the average of the major axis of a primary particle is 3.0 micrometers or less, and the size of the microcrystal measured with the X-ray diffraction method is characterized by being 100-1000A.
[Claim 2] The lithium cobalt multiple-oxide particle according to claim 1 whose specific surface area is 1-50m2 / g.
[Claim 3] At least one sort chosen from the group which the valence of cobalt becomes from the cobalt hydroxide which is trivalent, and oxy-cobalt hydroxide, And B, Mg, Si, Cu, Ce, Y, Ti, V, Mn, Fe, The compound which consists of at least one sort of elements chosen from the group which consists of nickel, Sn, Zr, Sb, Nb, Ru, Pb, Hf, Ta, La, Pr, and Nd The manufacture method of the lithium cobalt multiple-oxide particle characterized by performing heat-treatment after making it distribute in lithium-hydroxide solution.
[Claim 4] The manufacture method of a lithium cobalt multiple-oxide particle according to claim 3 that at least one sort of concentration chosen from the group which the valence of cobalt becomes from the cobalt hydroxide which is trivalent, and oxy-cobalt hydroxide converts into the concentration of a cobalt atom, and is 0.05 - 10 gram atom /L.
[Claim 5] The manufacture method of the lithium cobalt multiple-oxide particle according to claim 3 which teaches at least one sort chosen from the group which the valence of cobalt becomes from the cobalt hydroxide which is trivalent, and oxy-cobalt hydroxide, and lithium-hydroxide solution at a rate set to a (lithium) / (cobalt) =1 / 1 - 50/1 by the atomic ratio.
[Claim 6] The manufacture method of a lithium cobalt multiple-oxide particle according to claim 3, 4, or 5 that the temperature of heat-treatment is 100-374 degrees C.
[Claim 7] The rechargeable lithium-ion battery characterized by the bird clapper, using a lithium cobalt multiple-oxide particle according to claim 1 or 2 as a positive active material.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the lithium cobalt multiple-oxide particle which can be used as a charge of positive-electrode material of a rechargeable lithium-ion battery, its manufacture method, and the rechargeable lithium-ion battery which comes to use it.
[0002]
[Description of the Prior Art] A lithium cobalt multiple oxide is one of the material which attracts attention in recent years as a positive active material used for the rechargeable lithium-ion battery currently used for a notebook sized personal computer, PHS, the cellular phone, etc. as high power and a high-energy density cell. This thing For example, "application to composition [of spherical $LiCoO_2$ pulverized coal] and active material for lithium secondary batteries by ultrasonic spraying thermal decomposition method" [Ogiwara **** Yoshihiko Saito, the Yanagawa ****, Nobuo Ogata, Kokichi Yoshida, Masayuki Takashima, Yonezawa **** Yasuharu Mizuno, Norifumi Nagata, 101; journal OBU THE ceramic society OBU Japan written by Kenji Ogawa (Journalof the Ceramic Society of Japan), 1159-1163 pages (1993) (it is hereafter called "reference 1".) a group expressed with $LiMO_2$ (M is Cr, Mn, nickel, Fe, Co, or V among a formula.) as indicated by] -- it is in a compound, and since charge and discharge voltage is high especially, it is very suitable as a positive active material
[0003] In order to face as a positive active material of a rechargeable lithium-ion battery using such a lithium cobalt multiple oxide and to raise the performance, that to which composition of a lithium cobalt multiple oxide was changed, and the thing which has improved the physical property of a lithium cobalt multiple oxide are proposed. as that to which composition of a lithium cobalt multiple oxide was changed -- JP,3-127454,A -- composition of a lithium cobalt multiple oxide -- a lithium -- what was made rich is indicated JP,3-134969,A -- composition of a lithium cobalt multiple oxide -- cobalt -- what was made rich is indicated The thing which made the lithium cobalt multiple oxide dope metal ions, such as Mn, W, nickel, La, and Zr, is indicated by JP,3-201368,A, JP,4-328277,A, JP,4-319250,A, and JP,4-319260,A.
[0004] As what has improved the physical property of a lithium cobalt multiple oxide, what made specific surface area of a lithium cobalt multiple oxide below 2m2 / g is indicated by JP,4-56064,A, for example. In JP,4-33260,A and JP,5-94822,A, it is $LiCoO_2$. What gave the fixed grain-size property is indicated. In JP,3-272564,A and JP,5-36414,A, it is $LiCoO_2$. What was made into the crystal grain child who has specific X diffraction intensity is indicated.
[0005] A mean particle diameter D is $3< D<=9.0$ micrometers, and the lithium cobalt multiple oxide whose volume which a particle group with a particle size of 3-150 micrometers occupies is 75% or more of a whole product is indicated by JP,7-263028,A. The lithium cobalt multiple oxide which the n value in Rosin-Rammler particle size distribution (R-lambda) equipped with the shape of 2.0 or more corpuscular character is indicated by JP,7-262995,A.
[0006] By the way, in order to obtain high reliability and high repeatability to properties, such as stability over a negative electrode, internal resistance, sensitivity, and a speed of response in charge and discharge, as indicated by 1159 pages of reference 1 in using fine particles as a positive active material of a rechargeable lithium-ion battery, in submicron size, particle size distribution are narrow and need to carry out high-density restoration of the fine particles which are uniform composition. Especially the capacity that can be filled up with fine particles in a practical use cell is fixed. Therefore, many quantity of electricity can be taken out, so that restoration nature is high and the specific surface area of fine particles is large, supposing there is no difference in the cell performance per unit weight of a positive active material. For this reason, restoration nature is high, and it is very important that they are fine particles with a large specific surface area, when it has high reliability and high repeatability to many properties and the rechargeable lithium-ion battery of high power is manufactured.
[0007] However, since each above-mentioned lithium cobalt multiple oxide was compounded by carrying out solid phase reaction of sources of a lithium, such as a lithium carbonate, a lithium hydroxide, a peroxidation lithium, and a lithium nitrate, and the sources of cobalt, such as cobalt carbonate, cobalt hydroxide, cobalt oxide, and a cobalt nitrate,

at an elevated temperature, it was difficult for composition to be unable to become uniform easily, and for the particle size of a primary particle to become large, and to obtain what has a big specific surface area. Furthermore, since trituration processing needed to be performed and it became the latus powder of particle size distribution by such trituration processing in order to consider as the good powder of dispersibility suitable for production of the paste for positive electrodes in using it as a positive active material of a rechargeable battery since primary particles are welding mutually, it was difficult to narrow particle size distribution.
[0008]
[Problem(s) to be Solved by the Invention] In view of the above, this invention is submicron size suitable as fine particles for positive active materials for rechargeable lithium-ion batteries, its particle size distribution are narrow, and its specific surface area is large, and it aims at offering the lithium cobalt multiple-oxide particle which is uniform composition, its manufacture method, and the rechargeable lithium-ion battery which comes to use this.
[0009]
[Means for Solving the Problem] this invention is the following general formula (1).;
LiCo1-x Ax Oy (1)
(x express the rational number of 0-0.25 among a formula.) y expresses the rational number of 1.875-2.25. A B, Mg, Si, Cu, Ce, Y, Ti, V, Mn, Fe, nickel, at least one sort of elements chosen from the group which consists of Sn, Zr, Sb, Nb, Ru, Pb, Hf, Ta, La, Pr, and Nd are expressed It consists of a lithium cobalt multiple oxide expressed, and the average of the major axis of a primary particle is 3.0 micrometers or less, and the size of the microcrystal measured with the X-ray diffraction method is the lithium cobalt multiple-oxide particle which is 100-1000A. moreover, the cobalt hydroxide whose valence of cobalt of this invention is trivalent -- and In at least one sort and list which are chosen from the group which consists of oxy-cobalt hydroxide B, Mg, Si, Cu, Ce, Y, Ti, V, Mn, Fe, nickel, Sn, After distributing the compound which consists of at least one sort of elements chosen from the group which consists of Zr, Sb, Nb, Ru, Pb, Hf, Ta, La, Pr, and Nd in lithium-hydroxide solution, it is the manufacture method of the above-mentioned lithium cobalt multiple-oxide particle of performing heat-treatment. Furthermore, this invention is a rechargeable lithium-ion battery which comes to use the above-mentioned lithium cobalt multiple-oxide particle as a positive active material. this invention is explained in full detail below.
[0010] The lithium cobalt multiple-oxide particle of this invention is the following general formula (1).;
LiCo1-x Ax Oy (1)
(x express the rational number of 0-0.25 among a formula.) y expresses the rational number of 1.875-2.25. A expresses at least one sort of elements chosen from the group which consists of B, Mg, Si, Cu, Ce, Y, Ti, V, Mn, Fe, nickel, Sn, Zr, Sb, Nb, Ru, Pb, Hf, Ta, La, Pr, and Nd. It consists of a lithium cobalt multiple oxide expressed. Above x is the rational number of 0-0.25. Above y is the rational number of 1.875-2.25.
[0011] The lithium cobalt multiple-oxide particle of this invention is LiCoO2 which is equivalent to x= 0 and y= 2 in the above-mentioned general formula (1). You may consist of a lithium cobalt multiple oxide which has the composition expressed, and may consist of a lithium cobalt multiple oxide which has composition equivalent to 0< x<=0.25 and 1.875<=y<=2.25 in the above-mentioned general formula (1).
[0012] When it is what consists of a lithium cobalt multiple oxide which has composition equivalent to 0< x<=0.25 and 1.875<=y<=2.25 in the above-mentioned general formula (1), The lithium cobalt multiple-oxide particle of this invention At least one sort of atoms chosen from the group which consists of B, Mg, Si, Cu, Ce, Y, Ti, V, Mn, Fe, nickel, Sn, Zr, Sb, Nb, Ru, Pb, Hf, Ta, La, Pr, and Nd in addition to Co atom can be included.
[0013] As a lithium cobalt multiple oxide which has the above 0< x<=0.25 and composition equivalent to 1.875<=y<=2.25 For example, LiCo0.9 nickel 0.1O2, LiCo0.95V0.05O2.05, LiCo0.98V0.02O2.02, and LiCo0.85Mn 0.15O2, LiCo0.95Mn 0.05O2 and LiCo0.97Ti 0.03O2.015, LiCo0.97Cu 0.03O1.985, LiCo0.98Sb 0.02O2.02, LiCo 0.90B0.10O2, and LiCo0.95Mg 0.05O1.975, LiCo0.80Fe 0.20O2 and LiCo0.99Ta0.01O2.01 grade can be mentioned.
[0014] The crystal structure of the above-mentioned lithium cobalt multiple oxide is alpha-NaFeO 2 based on a stratified rock salt type. It is type and the X diffraction pattern is LiCoO2 of ASTM:No.36-1004. It is the same.
[0015] The average of the major axis of a primary particle of the lithium cobalt multiple-oxide particle of this invention is 3.0 micrometers or less. If it exceeds 3.0 micrometers, a particle becomes large, and since it is not desirable as a positive active material of a rechargeable lithium-ion battery, it will be limited to the above-mentioned range. Preferably, it is 0.3-2.0 micrometers.
[0016] The size of the microcrystal by which the lithium cobalt multiple-oxide particle of this invention was measured with the X-ray diffraction method is 100-1000A. The size of the above-mentioned microcrystal is computable from the formula of Following Scherrer based on measurement of an X-ray diffraction method.
[0017]
[Equation 1]

$$\varepsilon = 0.9 \cdot \frac{\lambda}{\beta_{1/2} \cdot \cos\theta}$$

[0018] epsilon expresses the size (A) of a microcrystal among a formula. lambda expresses measurement X-ray wavelength (A). beta1/2 A half peak width (radian) is expressed. theta expresses the Bragg angle (radian) of a diffraction line.

[0019] The specific surface area of the lithium cobalt multiple-oxide particle of this invention has desirable 1-50m2 / g. If many quantity of electricity cannot be taken out quickly but 50m2 / g is exceeded when specific surface area is too small in their being under 1m2 / g and it is used as a positive active material of a rechargeable lithium-ion battery, stable charge and discharge will be hard to be obtained. Claim 5

[0020] Since the lithium cobalt multiple-oxide particle of this invention has the size of the primary particle of above-mentioned within the limits, it can obtain high reliability and high repeatability to properties, such as stability over the negative electrode at the time of using it as a positive active material of a rechargeable lithium-ion battery, internal resistance, sensitivity, and a speed of response in charge and discharge. Moreover, since it can consider as the specific surface area of the above-mentioned range, when it is used as a positive active material of a rechargeable lithium-ion battery, it is stabilized and many quantity of electricity can be taken out.

[0021] In this invention the above-mentioned lithium cobalt multiple-oxide particle At least one sort chosen from the group which the valence of cobalt becomes from the cobalt hydroxide which is trivalent, and oxy-cobalt hydroxide, And B, Mg, Si, Cu, Ce, Y, Ti, V, Mn, Fe, After distributing the compound which consists of at least one sort of elements chosen from the group which consists of nickel, Sn, Zr, Sb, Nb, Ru, Pb, Hf, Ta, La, Pr, and Nd in lithium-hydroxide solution, it can manufacture by performing heat-treatment.

[0022] The valence of cobalt is trivalent and the above-mentioned cobalt hydroxide used for this invention is the following general formula (2).;

$Co(OH)_3$ and aH_2O (2)

It is come out and expressed. a is zero or more among a formula. The above-mentioned cobalt hydroxide can be obtained as sedimentation produced when alkali is added to trivalent cobalt (III) ammine-complex-salt solution.

[0023] After oxidizing the compound which is not limited especially as the above-mentioned oxy-cobalt hydroxide used for this invention, for example, has divalent cobalt, such as a cobalt nitrate, a cobalt chloride, and a cobalt sulfate, by the oxidizer, what was neutralized with alkali can be mentioned.

[0024] it limits especially as the above-mentioned oxidizer -- not having -- for example, air, oxygen, an ozone; permanganic acid ($HMnO_4$), and $MMnO_4$ etc. -- the salt; chromic acid (CrO_3) and $M_2Cr_2O_7$ which are expressed -- M_2CrO_4, $MCrO_3Cl$, and CrO_2Cl_2 etc. -- the related compound;F_2 expressed -- Cl_2, Br_2, and I_2 etc. -- halogen; -- H_2O_2 and Na_2O_2 -- BaO_2 etc. -- peroxide; -- pel oxo acid and $M_2S_2O_8$, M_2SO_5, and H_2CO_3 -- the salt; oxygen acid and MClO, and MBrO which are expressed with CH_3CO_3H etc., MIO and $MClO_3$, $MBrO_3$, MIO_3, $MClO_4$, MIO_4, $Na_3H_2IO_6$, and KIO_4 etc. -- the salt expressed can be mentioned M expresses an alkali-metal element among a formula.

[0025] It is not limited especially as the above-mentioned alkali, for example, solution, such as a lithium hydroxide, a potassium hydroxide, a sodium hydroxide, and an ammonium hydroxide, etc. can be mentioned.

[0026] The above-mentioned oxy-cobalt hydroxide can dissolve in water the compound which has divalent cobalt, such as a cobalt nitrate, a cobalt chloride, and a cobalt sulfate, can be made into solution, can add the above-mentioned oxidizer and the above-mentioned alkali, and can obtain them by performing neutralization and oxidization simultaneously. Moreover, after adding the above-mentioned alkali to the solution containing the compound which has the above-mentioned divalent cobalt and compounding divalent cobalt hydroxide, the above-mentioned oxy-cobalt hydroxide can also be obtained by adding an oxidizer and oxidizing. Furthermore, after adding the above-mentioned oxidizer in the solution containing the compound which has the above-mentioned divalent cobalt, the above-mentioned oxy-cobalt hydroxide can also be obtained by adding the above-mentioned alkali and neutralizing.

[0027] In this invention, at least one sort chosen from the group which consists of the above-mentioned cobalt hydroxide and oxy-cobalt hydroxide is distributed in the above-mentioned lithium-hydroxide solution. The above-mentioned lithium-hydroxide solution contains a lithium ion and a hydroxide ion in solution. In solution, this thing can be dissolved in water and can prepare the compound which can generate a lithium ion and a hydroxide ion, for example, a lithium hydroxide, a lithium oxide, a metal lithium, etc. "Lithium-hydroxide solution" means what dissolved in water and prepared the compound which can generate a lithium ion and a hydroxide ion in the above-mentioned solution among this specification. In this invention, the compound which can generate a lithium ion and the hydroxide ion in the above-mentioned solution is used as a source of a lithium.

[0028] Although especially the concentration in at least one sort of distributed liquid chosen from the group which consists of the above-mentioned cobalt hydroxide and oxy-cobalt hydroxide is not limited, usually, it is converted into

the concentration of a cobalt atom and its 0.05 - 10 gram atom / L are desirable. From the point of the operability in a manufacturing process, or economical efficiency, they are 0.1 - 5 gram atom /L more preferably.
[0029] After a reaction, since the preparation ratio of at least one sort chosen from the group which consists of the above-mentioned cobalt hydroxide and the above-mentioned oxy-cobalt hydroxide, and the above-mentioned lithium-hydroxide solution can collect the residual sources of a lithium, they should just be a (lithium) / (cobalt) >=1 in an atomic ratio. From the point of the operability in a manufacturing process, or economical efficiency, preferably, it is a (lithium) / (cobalt) =1 / 1 - 50/1, and it is a (lithium) / (cobalt) =1 / 1 - 20/1, and is a (lithium) / (cobalt) =1 / 1 - 10/1 still more preferably.
[0030] In the manufacture method of this invention, when the preparation ratio of at least one sort chosen from the group which consists of the above-mentioned cobalt hydroxide and the above-mentioned oxy-cobalt hydroxide, and the above-mentioned lithium-hydroxide solution is conversely set to a (lithium) / (cobalt) <1 by the atomic ratio in an above-mentioned case, the content of the cobalt in the lithium cobalt multiple-oxide particle obtained can be made [more] than the content of a lithium.
[0031] In the manufacture method of this invention further in the above-mentioned distributed liquid B, Mg, Si, By distributing the compound which consists of at least one sort of elements chosen from the group which consists of Cu, Ce, Y, Ti, V, Mn, Fe, nickel, Sn, Zr, Sb, Nb, Ru, Pb, Hf, Ta, La, Pr, and Nd In the above-mentioned general formula (1), the lithium cobalt multiple-oxide particle which has composition equivalent to 0< x<=0.25 can be obtained. It is not limited especially as the above-mentioned compound, for example, the simple substance of the above-mentioned element, a hydroxide, an oxide, etc. can be mentioned. These may be used independently and may use two or more sorts together. The addition of the above-mentioned compound is an atomic ratio among distributed liquid, and let it be the amount from which the rate of the atom of the above-mentioned element becomes 0.25 or less to the sum of a cobalt atom and the atom of the above-mentioned element in the above-mentioned compound.
[0032] In the manufacture method of this invention, since the one of reactivity where the concentration of the hydroxide ion in the above-mentioned distributed liquid is higher is good, you may add the compound which can generate a hydroxide ion further in the above-mentioned distributed liquid. It is not limited especially as a compound which can generate the above-mentioned hydroxide ion, for example, a sodium hydroxide, a potassium hydroxide, an ammonium hydroxide, etc. can be mentioned.
[0033] The heating temperature in the above-mentioned heat-treatment has desirable 60-500 degrees C. When a long time is taken to complete a reaction as it is less than 60 degrees C and it exceeds 500 degrees C, a water vapor pressure must become very high, the pressure resistance of a reaction container must be maintained, and a problem is in economical efficiency from the point of equipment cost. From the point of the operability in a manufacturing process, or economical efficiency, it is 100-374 degrees C more preferably. When heating temperature exceeds 100 degrees C, it is necessary to use a proof-pressure container as a reaction container, and to suppress boil of the above-mentioned water dispersion.
[0034] Although the reaction time in the above-mentioned heat-treatment changes with heating temperature, it is several minutes - several days. You may perform the above-mentioned heat-treatment, stirring distributed liquid.
[0035] In the manufacture method of this invention, reaction mixture can be cooled after the above-mentioned heat-treatment to the temperature in which separation operation is possible, sedimentation can be separated using the separation methods, such as filtration, and the powder of the target lithium cobalt multiple-oxide particle can be obtained by fully rinsing and drying. The temperature of the above-mentioned dryness will not be limited especially if the adsorption moisture of a lithium cobalt multiple-oxide particle can remove enough.
[0036] Moreover, you may give dry-type heat-treatment to the product after dryness if needed. Since the degree of crystallinity of the lithium cobalt multiple-oxide particle obtained can be raised further and the size of a primary particle can be adjusted by the above-mentioned dry-type heat-treatment, the lithium cobalt multiple-oxide particle corresponding to the desired cell property can be obtained. Before carrying out after collecting the lithium cobalt multiple-oxide particles obtained after dryness, and collecting, you may perform the above-mentioned dry-type heat-treatment simultaneously with a dryness process.
[0037] The liquid phase separated by the above-mentioned filtration etc. can be collected and reused. Moreover, it can also discard after processing.
[0038] Unlike the solid phase reaction in the elevated temperature conventionally used for manufacturing a lithium cobalt multiple-oxide particle, the manufacture method of this invention can manufacture the lithium cobalt multiple-oxide particle which a primary particle did not weld, and the size of submicron size is good and gathered. For this reason, there is no need for the trituration processing of a particle currently performed conventionally, and the narrow lithium cobalt multiple-oxide particle of a particle size distribution can be obtained.
[0039] By the manufacture method of this invention, composition is uniform and the lithium cobalt multiple-oxide particle excellent in the homogeneity of the crystal structure can be obtained. In this case, the size of the primary

particle of the above-mentioned lithium cobalt multiple-oxide particle is equivalent to the major axis of the above-mentioned crystal, and can set the average to 3.0 micrometers or less. Moreover, the size of the microcrystal of the above-mentioned lithium cobalt multiple oxide is 100-1000A, and that whose specific surface area is 1-50m2 / g can be obtained.

[0040] The above-mentioned lithium cobalt multiple-oxide particle is used for the rechargeable lithium-ion battery of this invention as a positive active material. The above-mentioned positive active material is usually used as a kneading paste which added, kneaded and obtained the electric conduction agent, the binder, the filler, etc. to the above-mentioned lithium cobalt multiple-oxide particle.

[0041] Especially if it is the electronic-conduction nature material which does not cause a chemical change in a rechargeable lithium-ion battery as the above-mentioned electric conduction agent, it will not be limited, for example, a natural graphite, an artificial graphite, carbon black, acetylene black, KETCHIEN black, a carbon fiber, a metal powder, a metal fiber, a polyphenylene derivative, etc. can be mentioned. These may be used independently and may use two or more sorts together. Although especially the addition of the above-mentioned electric conduction agent is not limited, its 1 - 50 % of the weight is usually desirable during the above-mentioned kneading paste. It is 2 - 30 % of the weight more preferably.

[0042] It is not limited especially as the above-mentioned binder, for example, a starch, polyvinyl alcohol, carboxymethyl-cellulose, hydroxypropylcellulose, regenerated-cellulose, diacetyl-cellulose polyvinyl-chloride, polyvinyl-pyrrolidone, tetrafluoroethylene, polyvinylidene-fluoride, polyethylene, polypropylene, and ethylene-propylene-diene copolymer (EPDM), sulfonation EPDM, a styrene butadiene rubber, a polybutadiene, a fluororubber, a polyethylene oxide, etc. can be mentioned. These may be used independently and may use two or more sorts together. Although especially the addition of the above-mentioned binder is not limited, its 1 - 50 % of the weight is usually desirable during the above-mentioned kneading paste. It is 2 - 30 % of the weight more preferably.

[0043] Especially if it is the fibrous material which does not cause a chemical change in a rechargeable lithium-ion battery as the above-mentioned filler, it will not be limited, for example, fiber, such as olefin system polymer; glass, such as polypropylene and polyethylene, and carbon, etc. can be mentioned. Although especially the addition of the above-mentioned filler is not limited, its 0 - 30 % of the weight is usually desirable during the above-mentioned kneading paste.

[0044] In the rechargeable lithium-ion battery of this invention, especially if used for the usual rechargeable lithium-ion battery as a negative-electrode electrode material, it will not be limited, for example, stainless steel, nickel, copper, titanium, aluminum, a baked carbon, etc. can be mentioned.

[0045] As a positive active material, the average of the major axis of a primary particle is 3.0 micrometers or less, the size of a microcrystal is 100-1000A, specific surface area is 1-50m2 / g, and since the particle size distribution is using the narrow lithium cobalt multiple-oxide particle, the rechargeable lithium-ion battery of this invention can obtain high reliability and high repeatability to properties, such as stability over a negative electrode, internal resistance, sensitivity, and a speed of response in charge and discharge.

[0046] the rechargeable lithium-ion battery of this invention -- for example, a notebook sized personal computer, a cellular phone, and a cordless phon -- it can be used suitable for medical equipment, such as electronic equipment; pacemakers, such as a cordless handset, a video movie, a liquid crystal television, an electric shaver, pocket radio, a headphone stereo cassette tape recorder, a backup power supply, and memory card, and a hearing-aid, etc.

[0047]

[Example] Although an example is hung up over below and this invention is explained to it in more detail, this invention is not limited only to these examples.

[0048] The manufacture examples 1-11 and the example 1 of comparison of a lithium cobalt multiple-oxide particle were carried out. Underwater, it dissolved, alkali neutralization of the source of cobalt shown in Table 1 and the cobalt substituted compound was carried out, oxidation treatment was performed, and cobalt hydroxide was obtained. Distribution and heat-treatment were underwater performed for the source of a lithium shown in the obtained cobalt hydroxide and Table 1, and the lithium cobalt multiple oxide was obtained. The kind of each cobalt concentration (a gram atom/L), a (lithium)/(cobalt) atomic ratio, and cobalt substituted compound and an amount (g), heat-treatment temperature, and heat-treatment time were shown in Table 1. Moreover, the mean particle diameter of the primary particle of the obtained lithium cobalt multiple-oxide particle, specific surface area, and the size of a microcrystal were shown in Table 2.

[0049] It was dropped at it, stirring sodium-hydroxide solution 1.1of two-mol / L L to cobalt-nitrate solution 1of 11 mol [of examples], and L L, and the slurry of cobalt hydroxide (II) precipitation was obtained. Air oxidation was performed, filtration rinsing of the obtained slurry was carried out, stirring for 48 hours blowing air into this slurry, and the cake of oxy-cobalt hydroxide (III) precipitation was obtained. Next, 2.5 mols of lithium hydroxides were mixed in the cake of the obtained oxy-cobalt hydroxide (III), ion exchange water was added to this mixture, and the whole

quantity was set to 670ml. This slurry was taught to the autoclave and hydrothermal processing was carried out in heat-treatment temperature [of 200 degrees C], and heat-treatment time 4 hours. After carrying out filtration rinsing of the slurry after the reaction end and making it dry at 100 degrees C, when the X diffraction pattern of the obtained powder was measured, it was checked that it is a cobalt acid lithium ($LiCoO2$).

[0050] It was dropped at them, stirring 110ml of sodium-hydroxide solution of two mols / L in 100ml of cobalt-nitrate solutions of 21 mols of examples, and L, and the slurry of cobalt hydroxide (II) precipitation was obtained. Air oxidation was performed, filtration rinsing of the obtained slurry was carried out, stirring for 48 hours blowing air into this slurry, and the cake of oxy-cobalt hydroxide (III) precipitation was obtained. Next, four mols of lithium hydroxides were mixed in the cake of the obtained oxy-cobalt hydroxide (III), ion exchange water was added to this mixture, and the whole quantity was set to 670ml. This slurry was taught to the autoclave and hydrothermal processing was carried out in heat-treatment temperature [of 130 degrees C], and heat-treatment time 24 hours. After carrying out filtration rinsing of the slurry after the reaction end and making it dry at 100 degrees C, when the X diffraction pattern of the obtained powder was measured, it was checked that it is a cobalt acid lithium.

[0051] It was dropped at them, stirring 550ml of sodium-hydroxide solution of two mols / L in 500ml of cobalt-nitrate solutions of 31 mols of examples, and L, and the slurry of cobalt hydroxide (II) precipitation was obtained. Air oxidation was performed, filtration rinsing of the obtained slurry was carried out, stirring for 48 hours blowing air into this slurry, and the cake of oxy-cobalt hydroxide (III) precipitation was obtained. Next, 2.5 mols of lithium hydroxides were mixed in the cake of the obtained oxy-cobalt hydroxide (III), ion exchange water was added to this mixture, and the whole quantity was set to 670ml. This slurry was taught to the autoclave and hydrothermal processing was carried out in heat-treatment temperature [of 250 degrees C], and heat-treatment time 2 hours. After carrying out filtration rinsing of the slurry after the reaction end and making it dry at 100 degrees C, when the X diffraction pattern of the obtained powder was measured, it was checked that it is a cobalt acid lithium.

[0052] It was dropped at them, stirring 550ml of sodium-hydroxide solution of two mols / L in 500ml of cobalt chloride solutions of 41 mols of examples, and L, and the slurry of cobalt hydroxide (II) precipitation was obtained. Air oxidation was performed, filtration rinsing of the obtained slurry was carried out, stirring for 48 hours blowing air into this slurry, and the cake of oxy-cobalt hydroxide (III) precipitation was obtained. Next, ten mols of lithium hydroxides were mixed in the cake of the obtained oxy-cobalt hydroxide (III), ion exchange water was added to this mixture, and the whole quantity was set to 670ml. This slurry was taught to the autoclave and hydrothermal processing was carried out in heat-treatment temperature [of 200 degrees C], and heat-treatment time 8 hours. After carrying out filtration rinsing of the slurry after the reaction end and making it dry at 100 degrees C, when the X diffraction pattern of the obtained powder was measured, it was checked that it is a cobalt acid lithium.

[0053] It was dropped at it, stirring sodium-hydroxide solution 1.1of two-mol / L L to cobalt-nitrate solution 1of 51 mol [of examples], and L L, and the slurry of cobalt hydroxide (II) precipitation was obtained. Air oxidation was performed, filtration rinsing of the obtained slurry was carried out, stirring for 48 hours blowing air into this slurry, and the cake of oxy-cobalt hydroxide (III) precipitation was obtained. Next, 2.5 mols of lithium hydroxides were mixed in the cake of the obtained oxy-cobalt hydroxide (III), ion exchange water was added to this mixture, and the whole quantity was set to 670ml. This slurry was taught to the autoclave and hydrothermal processing was carried out in heat-treatment temperature [of 300 degrees C], and heat-treatment time 1 hour. After carrying out filtration rinsing of the slurry after the reaction end and making it dry at 100 degrees C, when the X diffraction pattern of the obtained powder was measured, it was checked that it is a cobalt acid lithium.

[0054] It was dropped at it, stirring sodium-hydroxide solution 1.1of two-mol / L L to cobalt-sulfate solution 1of 61 mol [of examples], and L L, and the slurry of cobalt hydroxide (II) precipitation was obtained. Air oxidation was performed, filtration rinsing of the obtained slurry was carried out, stirring for 48 hours blowing air into this slurry, and the cake of oxy-cobalt hydroxide (III) precipitation was obtained. Next, 2.5 mols of lithium oxides were mixed in the cake of the obtained oxy-cobalt hydroxide (III), ion exchange water was added to this mixture, and the whole quantity was set to 670ml. This slurry was taught to the autoclave and hydrothermal processing was carried out in heat-treatment temperature [of 200 degrees C], and heat-treatment time 4 hours. After carrying out filtration rinsing of the slurry after the reaction end and making it dry at 100 degrees C, when the X diffraction pattern of the obtained powder was measured, it was checked that it is a cobalt acid lithium.

[0055] It was dropped at it, stirring sodium-hydroxide solution 1.1of two-mol / L L to mixed-solution 1L of the cobalt nitrate of 70.8 mols of examples, and L, and 0.2 mols / L nickel nitrate, and the slurry of cobalt hydroxide (II) precipitation was obtained. Air oxidation was performed, filtration rinsing of the obtained slurry was carried out, stirring for 48 hours blowing air into this slurry, and the cake of mixed-water oxide precipitation was obtained. Next, two mols of lithium hydroxides were mixed in the cake of the obtained hydroxide, ion exchange water was added to this mixture, and the whole quantity was set to 670ml. This slurry was taught to the autoclave and hydrothermal processing was carried out in heat-treatment temperature [of 200 degrees C], and heat-treatment time 4 hours. After

carrying out filtration rinsing of the slurry after the reaction end and making it dry at 100 degrees C, when the X diffraction pattern of the obtained powder was measured, the single X diffraction pattern was shown and it was checked that it is a cobalt nickel acid lithium.

[0056] To mixed-solution 1L of the cobalt nitrate of 80.8 mols of examples, and L, and 0.2 mols / L iron nitrate, it is 30 % of the weight H2 O2. It was dropped stirring 60ml of solutions, and oxidized. It was dropped stirring sodium-hydroxide solution 1.1of two-mol / L L in this solution, filtration rinsing of the obtained slurry was carried out, and the cake of mixed-water oxide precipitation was obtained. Next, two mols of lithium hydroxides were mixed in the cake of the obtained hydroxide, ion exchange water was added to this mixture, and the whole quantity was set to 670ml. This slurry was taught to the autoclave and hydrothermal processing was carried out in heat-treatment temperature [of 200 degrees C], and heat-treatment time 4 hours. After carrying out filtration rinsing of the slurry after the reaction end and making it dry at 100 degrees C, when the X diffraction pattern of the obtained powder was measured, the single X diffraction pattern was shown and it was checked that it is a cobalt ferric acid lithium.

[0057] It was dropped at it, stirring 600ml of sodium persulfates of one mol / L to mixed-solution 1L of the cobalt nitrate of 90.9 mols of examples, and L, and a 0.1 mols / L copper nitrate, and oxidized. It was dropped stirring sodium-sodium-hydroxide solution 1.1of two-mol / L L in this solution, filtration rinsing of the obtained slurry was carried out, and the cake of mixed-water oxide precipitation was obtained. Next, 2.25 mols of lithium hydroxides were mixed in the cake of the obtained hydroxide, ion exchange water was added to this mixture, and the whole quantity was set to 670ml. This slurry was taught to the autoclave and hydrothermal processing was carried out in heat-treatment temperature [of 200 degrees C], and heat-treatment time 4 hours. After carrying out filtration rinsing of the slurry after the reaction end and making it dry at 100 degrees C, when the X diffraction pattern of the obtained powder was measured, the single X diffraction pattern was shown and it was checked that it is a cobalt **** lithium.

[0058] It was dropped at it, stirring sodium-hydroxide solution 2.2of two-mol / L L to mixed-solution 2L of the cobalt nitrate of 100.95 mols of examples, and L, and 0.05 mols / L vanadium chloride, and the slurry of cobalt hydroxide (II) precipitation was obtained. Air oxidation was performed, filtration rinsing of the obtained slurry was carried out, stirring for 48 hours blowing air into this slurry, and the cake of mixed-water oxide precipitation was obtained. Next, 2.85 mols of lithium hydroxides were mixed in the cake of the obtained hydroxide, ion exchange water was added to this mixture, and the whole quantity was set to 670ml. This slurry was taught to the autoclave and hydrothermal processing was carried out in heat-treatment temperature [of 200 degrees C], and heat-treatment time 4 hours. After carrying out filtration rinsing of the slurry after the reaction end and making it dry at 100 degrees C, when the X diffraction pattern of the obtained powder was measured, the single X diffraction pattern was shown and it was checked that it is a cobalt vanadium acid lithium.

[0059] 200 arbitrary primary particles were selected out of the electron microscope photograph taken using the measurement scanning electron microscope (JSM-840F, JEOL Co., Ltd. make) of a mean particle diameter, and the weighted average of the major axis was made into the mean particle diameter.

It measured using the measurement surface-area measuring device (Monosorb, product made from Quontachrome) of specific surface area.

[0060] the X diffraction was presented with the measurement profit **** lithium cobalt multiple-oxide particle of the size of a microcrystal, and size [of a microcrystal] epsilon (A) was computed by the following formula from Bragg angle [of measurement X-ray wavelength lambda(A) half-peak-width beta1 / 2 (radian), and a diffraction line] theta (radian)

[0061]

[Equation 2]

$$\varepsilon = 0.9 \cdot \frac{\lambda}{\beta_{1/2} \cdot \cos\theta}$$

[0062]

[Table 1]

	コバルト源	酸化剤	リチウム源	コバルト濃度(グラム原子/L)	Li/Co (原子比)	A元素化合物		加熱処理温度(℃)	加熱処理時間(時間)	リチウムコバルト複合酸化物組成式
						種類	量(g)			
実施例1	$Co(NO_3)_2$	空気	LiOH	1.5	2.5	--	--	200	4	$LiCoO_2$
実施例2	$Co(NO_3)_2$	空気	LiOH	0.15	40	--	--	130	24	$LiCoO_2$
実施例3	$Co(NO_3)_2$	空気	LiOH	0.75	5	--	--	250	2	$LiCoO_2$
実施例4	$CoCl_2$	空気	LiOH	0.75	20	--	--	200	8	$LiCoO_2$
実施例5	$Co(NO_3)_2$	空気	LiOH	1.5	2.5	--	--	300	1	$LiCoO_2$
実施例6	$Co(SO_4)_2$	空気	Li_2O	1.5	2.5	--	--	200	4	$LiCoO_2$
実施例7	$Co(NO_3)_2$	空気	LiOH	1.2	2	$Ni(NO_3)_2$	58	200	4	$LiCo_{0.8}Ni_{0.2}O_2$
実施例8	$Co(NO_3)_2$	H_2O_2	LiOH	1.2	2	$Fe(NO_3)_2$	81	200	4	$LiCo_{0.8}Fe_{0.2}O_2$
実施例9	$Co(NO_3)_2$	$Na_2S_2O_8$	LiOH	1.34	2.25	$Cu(NO_3)_2$	24	200	4	$LiCo_{0.9}Cu_{0.1}O_{1.95}$
実施例10	$Co(NO_3)_2$	空気	LiOH	2.84	1.5	VCl_3	8	200	4	$LiCo_{0.97}V_{0.03}O_{2.03}$

[0063] Dry type heat-treatment was further performed for the lithium cobalt multiple-oxide particle obtained in the example 11 example 1 at 500 degrees C for 2 hours, and the lithium cobalt multiple-oxide particle was obtained. The mean particle diameter of the primary particle of the obtained lithium cobalt multiple-oxide particle, specific surface area, and the size of a microcrystal were shown in Table 2.
[0064] The lithium cobalt multiple-oxide particle was obtained by calcinating at 900 degrees C and performing solid phase reaction, using cobalt oxide as a source of cobalt, using a lithium carbonate as a source of example of comparison 1 lithium. The mean particle diameter of the primary particle of the obtained lithium cobalt multiple-oxide particle, specific surface area, and the size of a microcrystal were shown in Table 2.
[0065]
[Table 2]

	平均粒径 (μm)	比表面積 (m^2/g)	結晶子サイズ (Å)
実施例1	0.3	11	300
実施例2	0.1	41	150
実施例3	0.2	20	200
実施例4	0.15	25	180
実施例5	2	1	800
実施例6	0.3	10	320
実施例7	0.3	8	350
実施例8	0.2	30	160
実施例9	0.05	47	120
実施例10	0.3	8	330
実施例11	0.3	9	400
比較例1	5.0	0.5	1100

[0066] The electron microscope photograph of the lithium cobalt multiple-oxide particle obtained in the example 1 was shown in drawing 1 . Moreover, the X diffraction chart of the lithium cobalt multiple-oxide particle obtained in the example 1 was shown in drawing 2 .
[0067] The weight ratio of 87:6.5:6.5 is sufficient, the lithium cobalt multiple oxide obtained in the manufacture example 12 example 1 of a rechargeable lithium-ion battery, acetylene black, and Teflon are kneaded, it applies to a pure stainless steel mesh (20mmphi) uniformly, and they are after that and 200 kg/cm2. After being stuck by pressure, it dried at 150 degrees C under reduced pressure for about 17 hours, and the positive electrode was produced. As a negative electrode, the metal lithium foil (20mmphi, 0.2mm thickness) was used, and the nonwoven fabric and the

polypropylene microfilm were used as a separator. Moreover, the electrolytic solution is $LiClO_4$ of 1M. What set moisture to 20 ppm or less was sunk in and used for the separator with a propylene carbonate solution and mixed liquor (1:1) with 1 and 2-dimethoxyethane. It included in the cell which showed these components to drawing 3 .
[0068] The cell produced by the above-mentioned method is used, and it is 1.0 mA/cm2. With fixed current, while cell voltages were 4.2-2.0V, charge and discharge were repeated. Consequently, initial capacity is 155 mAh/g and it turns out that the service capacity of 50 cycle eye is maintaining 89% of capacity of 1 cycle eye.
[0069]
[Effect of the Invention] Since this invention is as above-mentioned, it is submicron size, and particle size distribution are narrow, and specific surface area is large, and it is uniform composition, and the lithium cobalt multiple-oxide particle which can be suitably used as a positive active material of a rechargeable lithium-ion battery can be obtained efficiently. Moreover, charge and discharge voltage can be high, can take out many quantity of electricity, and can use the rechargeable lithium-ion battery using this lithium cobalt multiple-oxide particle as a positive active material suitable for electronic equipment, medical equipment, etc.

[Translation done.]